SCIREA Journal of Chemistry

http://www.scirea.org/journal/Chemistry

June 20, 2017

Volume 2, Issue 3, June 2017

Synthesis and Structure of A Liquid Crystal Compound: 1,4-bis(2,2,6,6-tetramethylpiperidin-4-yl)benzene

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Abstract

The title compound, $C_{24}H_{40}N_2$, was synthesized via etherification, Grignard reaction, dehydration and hydrogenation to produce 1,4-bis(2,2,6,6-tetramethylpiperidin-4-yl)benzene with a purity of more than 99. 95%. The overall yield was 70%. The structure of the target compound was confirmed by IR and single-crystal X-ray diffraction.

Keywords: 1,4-bis(2,2,6,6-tetramethylpiperidin-4-yl)benzene; Crystalline structure; Liquid crystal.

1. Introduction

Liquid crystal (LC) is a special kind of material. It features two aspects: one is that the arrangement of LC molecules is responsible for the magnetic, mechanical, and electric properties;

the other is that it has some fluid properties of the liquid [1]. Due to these characteristics, LC are extensively exploited in many areas of science and engineering, especially in electro-optic devices [2,3] The ability of LC depends on a number of factors, such as reactant molecular length, the mesophase type, flexibility and polarizability. In other word, the anisotropic physical properties of mesogenic materials strongly depend on the chemical structure of the molecules.

In recent decades there has been much interest in the synthesis and characterization of heterocyclic compounds as liquid crystals, because they can impart lateral and/or longitudinal dipoles combined with changes in the molecular shape [4,5]. The incorporation of heteroatoms result in considerable changes in the corresponding liquid crystalline phases and/or in the physical properties of the observed phases, as most of the heteroatoms (S, O, and N) commonly introduced are more polarizable than carbon [6,7] Recently, Yeap and Mohammad reported the synthesis and characterization of a large number of heterocyclic oxazepine LC materials that exhibited one phase, N (nematic) phase [8-10]. On the other hand, as one of the most widely used liquid crystal monomers, the hexamethylene alkyl benzene has been applied to many fields, such as the Thin Film Transistor (TFT) liquid crystal, the first grade tiny Twisted Nematic (TN), the Super Twisted Nematic (STN) and etc.

To sum up, in the process of expanding LC materials with good performance, in this paper we report the syntheses and crystal structure of a novel LC molecule 1,4-bis(2,2,6,6-tetramethylpiperidin-4-yl)benzene (**1**) in which heteroatom N is introduced in a ramification of hexamethylene benzene.

2. Experimental

All chemicals were of analytical reagent grade and used without further purification.

2.1. Physical Measurements

The Infrared (IR) spectra were recorded as KBr pellets on a Bruckr 27 FT-IR spectrometer.

2.2. X-ray crystallography and structure solution

Single-crystal X-ray diffraction data for **1** were collected on a Bruker Smart Apex II diffractometer, equipped with 1 K CCD instrument, using a graphite monochromator with Mo-Kα

radiation (λ = 0.71073 Å) at room temperature. Cell parameters were determined using SMART software [11]. Data reduction and correction were performed using SAINTPlus [12]. Absorption corrections were made via SADABS program [13].

The structures were solved by direct methods with the program package [14]. All non-H atoms were refined anisotropically. The H atoms attached to C and N atoms were added theoretically and treated as riding on the concerned atoms. The final cycle of full-matrix least-squares refinement was based on observed reflections and variable parameters. A summary of the crystallographic data and data collection and refinement parameters for the compound are provided in Table 1. The selected bond lengths and bond angles are listed in Table 2. Crystallographic data in CIF format were deposited with the Cambridge Crystallographic Data Center as CCDC No. 1549561.

Table 1 Crystal data and structure refinement of 1

Complex	**1**
CCDC number.	1549561
Empirical formula	$C_{24}H_{40}N_2$
Color/shape	Colourless/block
Formula weight	356.58
Radiation type	Mo Kα
Temperature(K)	296 (2)
Wavelength(Å)	0.71073
Crystal system	Monoclinic
Crystal size (mm)	0.35×0.33×0.30
Space group	$P2_1/c$
Unit cell dimensions	
a(Å)	7.734(1)
b(Å)	13.156(1)
c(Å)	12.056(2)
β(°)	114.440(1)
Volume(Å^3)	1116.8(2)

Z	2
Calculated density (mg mm^{-3})	1.060
Absorption coefficient(mm^{-1})	0.061
F_{000}	396
θ range for data collection	3.097 ~ 25.047
Index ranges	-8<h<9, -15<k<15, -14<l<14,
Reflections collected	1909
Independent reflections	1446 [R_{int} = 0.0376]
Completeness (%)	96.6
Absorption correction	Multi-scan
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1909/0/124
Goodness-of-fit on F^2	1.059
Final R indices [$I>2\sigma(I)$]	R_1= 0.0716, wR_2= 0.2292
R indices (all data)	R_1= 0.0892, wR_2= 0.2577
Largest diff. peak and hole(e ·$Å^{-3}$)	0.396 and -0.479

Table 2 Selected bond lengths (Å) and angles (°) for 1

N(1)-C(7)	1.485(3)	C(6)-C(9)	1.532(4)
N(1)-H(1A)	0.8600	C(6)-C(10)	1.543(4)
C(1)-C(2)	1.385(3)	C(7)-C(11)	1.535(4)
C(1)-C(3)#1	1.391(3)	C(7)-C(12)	1.535(4)
C(2)-C(3)	1.398(3)	C(7)-C(8)	1.539(3)
C(2)-C(4)	1.519(3)	C(4)-C(8)	1.531(3)
C(3)-C(1)#1	1.391(3)	C(5)-C(6)	1.540(3)
C(4)-C(5)	1.524(3)		
C(1)-C(2)-C(4)	121.22(19)	C(1)-C(2)-C(3)	117.1(2)
C(3)-C(2)-C(4)	121.6(2)	C(2)-C(4)-C(5)	113.41(19)
C(1)#1-C(3)-C(2)	121.1(2)	C(2)-C(4)-C(8)	110.82(17)

C(2)-C(1)-C(3)#1	121.8(2)	C(4)-C(5)-C(6)	113.6(2)
C(6)-N(1)-C(7)	119.87(18)	C(5)-C(4)-C(8)	108.81(18)
N(1)-C(6)-C(9)	106.10(19)	N(1)-C(7)-C(12)	106.4(2)
N(1)-C(6)-C(5)	111.33(18)	C(11)-C(7)-C(12)	108.2(2)
C(9)-C(6)-C(5)	109.2(2)	N(1)-C(7)-C(8)	111.07(18)
N(1)-C(6)-C(10)	111.4(2)	C(11)-C(7)-C(8)	110.33(19)
C(9)-C(6)-C(10)	107.5(2)	C(12)-C(7)-C(8)	109.03(19)
C(5)-C(6)-C(10)	111.1(2)	C(4)-C(8)-C(7)	113.23(17)
N(1)-C(7)-C(11)	111.68(19)		

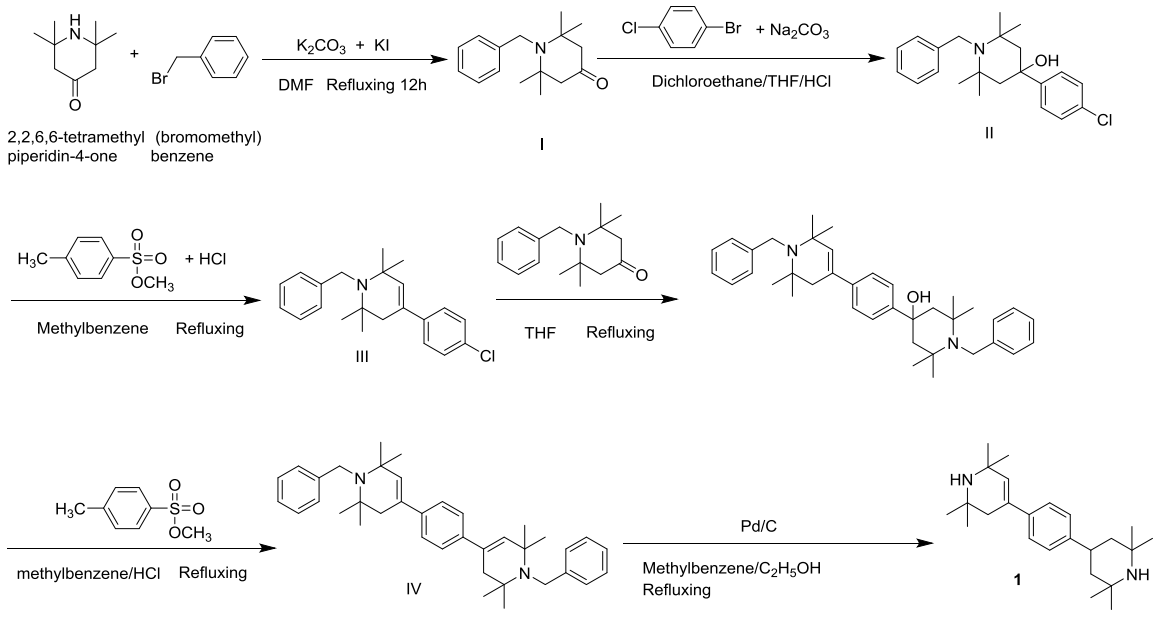
Symmetry transformations used to generate equivalent atoms: #1 -x+1, -y+2, -z+2.

3. Results and Discussion

3.1. The Synthesis of The Liquid Crystalline

The synthesis route of compound **1** was given in Scheme 1.

Scheme 1 Diagram showing the synthesis of compound **1**.



Liquid crystalline **1** was prepared firstly by the reaction of 2,2,6,6-tetramethylpiperidin-4-one (1 mol) and (bromomethyl)benzene (1 mol) in DMF (1 L) refluxing for 12 h, with the addition of K_2CO_3 (18 mol) and KI (0.1 mol). The reaction mixture was extracted by a dichloromethane/H_2O mixture with 1:2 volume ratio, concentrated, filtrated and freezed in -20℃ for 12 h, then

flavescens powder of 1-benzyl-2,2,6,6-tetramethylpiperidin-4-one (I) were obtained. Secondly, added 1-bromo-4-chlorobenzene (0.5 mol), (I) (0.2 mol) and Na_2CO_3 (0.6mol) to a THF/ dichloromethane/HCl (5 : 30 : 2 volume ratio) mixture, reacted, extracted by the dichloromethane and concentrated, then flavescens powder of 1-benzyl-4-(4-chlorophenyl)-2,2,6,6-tetramethylpiperidin-4-ol (II) were obtained. Thirdly, added methyl 4-methylbenzenesulfonate (0.03 mol) and concentrated hydrochloric acid (0.003 mol) to (II) (0.2 mol), refluxing in 500 mL methylbenzene, concentrated and recrystallized, then white powder of 1-benzyl-4-(4-chlorophenyl)-2,2,6,6-tetramethyl-1,2,3,6-tetrahydropyridine (III) were obtained. Fourthly, mixed 0.045 mol (I) and 0.03 mol (III) in 20 mL THF, refluxing for 2 h, followed by the addition of methyl 4-methylbenzenesulfonate (0.03 mol), concentrated hydrochloric acid (0.008 mol) and 1 L methylbenzene to the reaction mixture for concentration, then obtained 1,4-bis(1-benzyl-2,2,6,6-tetramethyl-1,2,3,6-tetrahydropyridin-4-yl)benzene (IV). The last step, dissolved 0.01 mol (IV) in a methylbenzene/ethanol mixture with 7: 1 volume ratio, with the addition of 0.01 mol Pd/C, and refluxed for 6 h. The raw product was purified by column chromatography. The final recrystallization was performed by cooling a boiling methylbenzene solution of the product to 60 ℃, and freezed in -20℃ for 4 h, then white powder of end-product 1,4-bis(2,2,6,6-tetramethylpiperidin-4-yl)benzene (**1**) were obtained in 70% yield. Single crystals, in the form of block, were obtained by slow evaporation from mother solution. IR (υ/cm^{-1}, s for strong, m medium, w weak): 3422w, 2993m, 2967s, 2953s, 2902s, 2837w, 1507m, 1461m, 1448m, 1423w, 1367s, 1306w, 1281m, 1237s, 1180m, 1159m, 1109m, 1091m, 1012m, 836s, 784w, 763m, 687s, 570s, 508m, 482m.

3.2 Description of the structure of compound 1

Single-crystal X-ray diffraction revealed that compound **1** crystallized in the monoclinic with number 14 of space group. Selected bond lengths and bond angles of compound **1** were listed in Tables 2. The asymmetric unit consisted of one crystallographically independent tetramethylpiperidine molecule and half a benzene ring. The whole molecular structure was shown in Figure 1. The tetramethylpiperidine rings adopts the chair conformation, and the dihedral angle between the back and seat is 49.8 °. The tetramethylpiperidine and benzene rings are almost perpendicular, producing a dihedral angle of 99.1 °. All C-C and C-N bond distances and the bond angles are typical and comparable to those observed in the similar results [15-17].

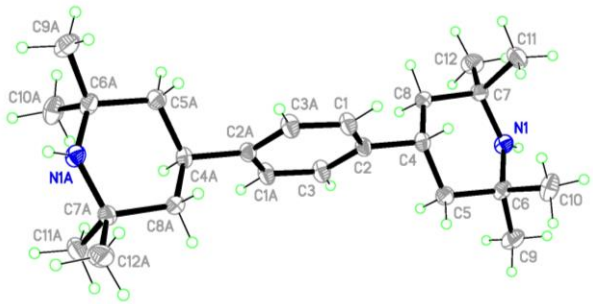


Figure. 1 The whole molecular structure of compound 1 and displacement ellipsoids are drawn at the 30% probability (Symmetry codes: A -x+1, -y+2, -z+2).

Sheets of layered molecules are formed by lattice translations in the plane (a, b) (Figure. 2a)). The sheets are parallel to the lattice planes (0 0 k) and have equations z = 0 and y = 1/2 (shown in Figure. 2b)).

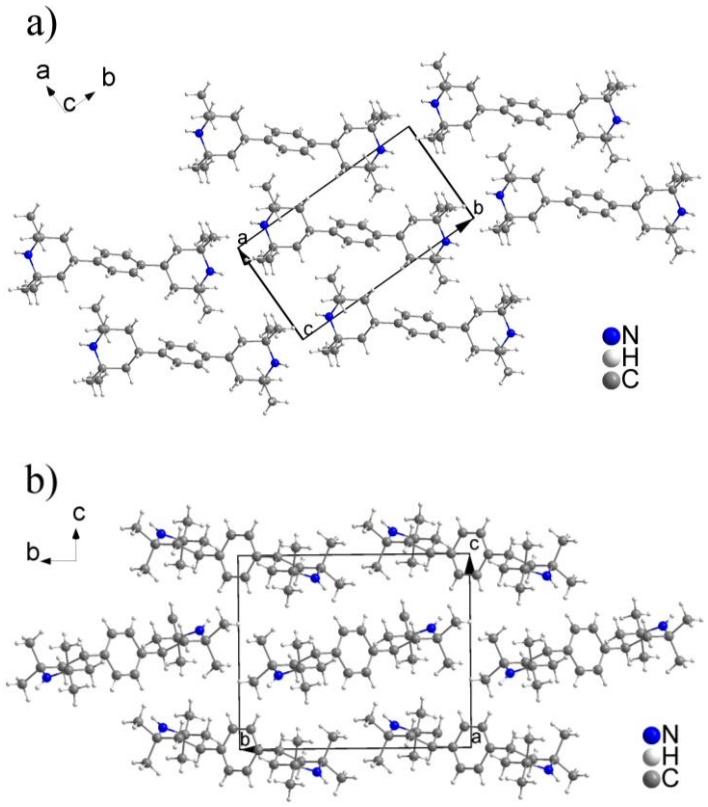


Figure. 2 a) A sheet of molecules of 1 viewed down *c*; b) the same sheet viewed down *a*.

4. Conclusions

We have synthesized and structurally characterized a novel liquid crystal compound 1,4-bis(2,2,6,6-tetramethylpiperidin-4-yl)benzene. It was synthesized through etherification, Grignard reaction, dehydration and hydrogenation process with a purity of more than 99. 95%. The overall yield was 70%. The crystal structure showed the layered sheets from *c* direction.

Supplementary Materials

The cif file of compound **1** was deposited with the Cambridge Crystallographic Data Center (CCDC 1549561). The data can be obtained free of charge from authors or the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; FAX: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk.

References

[1] S. W. Kang, X. Y. Zhang, Applied. Optics. 2016, 55, 12, 3333-3338.

[2] R.B. Meyer, L. Liebert, L. Strezelecki, P. Keller, J. Phys. Lett. 1975, 30, 69.

[3] S. Patari, A. Nath, J. Mol. Liq. 2017, 230, 247-253.

[4] A.S. Matharu, D.C. Asman, Liq. Cryst. 2007, 34, 1317.

[5] H. Gallardo, R. F. Magnago, A. J. Bortoluzzi, Liq. Cryst. 2001, 28, 1343.

[6] C. K. Lai, Y. Ke, J. S. C. Shen, W. Li, Liq. Cryst. 2002, 29, 915.

[7] A. T. Mohammada, G. Y. Yeap, H. Osman, J. Mol. Struct. 2015, 1087, 88-96.

[8] G. Y. Yeap, A.T. Mohammad, H. Osman, J. Mol. Struct. 2010, 982, 33.

[9] G. Y. Yeap, A.T. Mohammad, H. Osman, Mol. Cryst. Liq. Cryst. 2012, 552, 177.

[10] A. T. Mohammad, G. Y. Yeap, H. Osman, Aust. J. Basic. Appl. Sci. 2011, 5, 551.

[11] G. Candiano, A. Petretto, M. Bruschi, L. Santucci, V. Dimuccio, M. Prunotto, R. Gusmano, A. Urbani and G. M. Ghiggeri, J. Proteomics, 2009, 73, 188.

[12] Y. Cai, Q. J. Xie, A. H. Zhou, Y. Y. Zhang and S. Z. Yao, J. Biochem. Biophys. Methods, 2001, 47, 209.

[13] R. H. Blessing, Acta Crystallogr., Sect. A: Found. Crystallogr., 1995, 51, 33.

[14] G. Sheldric , Acta Cryst. A, 2015, 71**,** 3-8.

[15] Effendy, P. C. Junk, C. J. Kepert, L. M. Louisc, T. C. Moriena, B. W. Skeltona, A. H. White, Z. Anorg. Allg. Chem. 2006, 632, 1312-1325.

[16] B. Ahrens, P. G. Jones, A. K. Fischer, Eur. J. Inorg. Chem. 1999, 1103-1110.

[17] R. Tacke, R. Bertermann, C. Burschka, S. Dragota, M. Penka, I. Richter, J. Am. Chem. Soc. 2004, 126, 14493-14505.